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SOLUBILITY STUDIES IN ALKALI METALS

SEVENTH QUARTERLY REPORT

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SOLUBILITY STUDIES OF ULTRA PURE TRANSITION ELEMENTS IN ULTRA PURE ALKALI METALS

SEVENTH QUARTERLY REPORT

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By
R.L. McKISSON
R.L. EICHELBERGER

Prepared for
National Aeronautics and Space Administration
Lewis Research Center

Project Management
NASA-Lewis Research Center
Space Power Systems Division
R. A. Lindberg

ATOMICS INTERNATIONAL
A DIVISION OF NORTH AMERICAN AVIATION, INC.
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SOLUBILITY STUDIES OF ULTRA PURE TRANSITION ELEMENTS AND COMPOUNDS IN ULTRA PURE ALKALI METALS

I. INTRODUCTION

The purposes of this study are to define the solution process and to determine the equilibrium solubility of highly purified transition metals and selected compounds in highly purified liquid alkali metals. The material combinations which are to be considered for the solution studies are: iron, niobium, tantalum, molybdenum, tungsten, zirconium, rhenium, vanadium, hafnium, beryllium oxide, niobium monoxide, tantalum monoxide, zirconium dioxide, zirconium carbide, vanadium monoxide, oxygen-saturated zirconium, and oxygen-saturated hafnium with liquid potassium, and niobium and beryllium oxide with liquid lithium. Specifc combinations from the above list will be selected, and it is expected that some combinations will not be investigated.

The studies to be made include the measurement of solubility in the alkali metal at temperatures up to 1200°C, coupled with the investigation of the rate-controlling step and its energy of activation.

It is the goal of this study to develop solubility data for well-characterized experimental systems, in which the number and range of complicating variables are minimized, in the hope that such data will not only further the understanding of these processes in alkali metal systems, but will also be of use in the materials selection and design of space electrical power system components.

II. SUMMARY

Solubility testing is continuing, and data have now been obtained for the solution of high purity iron, niobium, and molybdenum in high purity potassium. The problem, noted in the earlier reports, of the potassium retention within the crucible-collector sub-assembly has been resolved by the use of a nickel braze which seals the joint. A modification of the quench apparatus has been made, and the new water-cooled device is much more effective than the chill-blocks previously used. Cooling of the sample capsule to below the melting point of potassium is now achieved in less than 20 minutes. This tends to limit the time during which the dissolved solute may have the mobility required to deposit on, and to diffuse into, the collector walls.

Tentative values for the solubility of very pure metals in potassium containing 14 wppm oxygen are: for iron at 1000°C, 80 wppm, for niobium at 1000°C, 15 wppm; and for molybdenum at 1000°C, 3 wppm.

III. TECHNICAL PROGRAM

Solubility Testing

Solubility testing has been the principal activity during the quarter. The test equipment has operated smoothly and the rate of performing experiments averages about 2-1/2 per week. However, a difficulty was experienced in one of the tests (#346) when the platinum-rhodium thermocouples became firmly attached to the capsule. This tendency had been noted in one of the earlier runs but, although some of the thermocouples were broken at the end of the run, the completion of the test was not affected. In run #346, the tenacity of the bonding was greater and as a result, the TZM shaft, which supports the capsule during test, was broken during the attempt to invert the capsule at the end of the test. The repair of the TZM shaft was effected by arc welding, using a Mo-Re filler rod in a welding dry-box, under purified argon*. As a corrective measure to prevent repetition of the sticking of the thermocouples, bands of 0.002-inch tantalum foil are now fastened to the capsules so that the thermocouples bear on them, as shown in Figure 1. In order to ensure that the thermocouple junctions were not contaminated with molybdenum, those which showed evidence of sticking were cut back about an inch and re-formed. Since the use of the tantalum bands was begun, no evidence of thermocouple sticking has been observed. This is taken as sufficient evidence that there are no deleterious interactions under our test conditions at 1200°C. However, it does seem likely that 1200°C would be the upper limit of usefulness of this combination and that at higher temperatures a refractory metal thermocouple would be required.

A second problem arose with the furnace in that the original tantalum heating element required replacement. During the trimming operation, a small tear was formed. Consequently, a local hot spot developed, and the element became deteriorated locally after about 150 hours of intermittent service. The replacement heater consisted of two uniform width strips of 0.002-inch tantalum foil which were spot welded to 0.030-inch thick end fixtures. The equivalent of the trimmed element was effected by using a diamond shaped patch spot welded to the central zone of each heater element leg.

*Through the courtesy of the Vacuum Atmospheres Corporation.

A third operating problem was found in that the RYE manipulators began to show signs of wear. These accessories operate very satisfactorily when they are properly adjusted and are clean. The problem is that the jaw action becomes hard to control after they have been in service for a few days. The jaw operates through a cam action, and the cam and cam follower are presently made of type 304 stainless steel. During the gripping action, there is a substantial force at the cam surface and the parts tend to wear and gall. Therefore, it is necessary to periodically remove each manipulator and re-surface the cam parts. The manufacturer has been advised of this difficulty and when suitable replacement parts become available, the faulty ones will be replaced.

A change has been made in the quench apparatus. The earlier design was a clam-shell block with one movable half which was closed over the capsule to effect the quenching. Because of the variation in the way in which the various capsules seated themselves in the block, there was a variation in the quenching rate. Further, the blocks were not cooled so that their temperatures rose slowly during the test periods. Because these factors produced wide variations in the efficacy of the quenching operation, a means of obtaining a more uniform and more rapid quenching operation was sought. The result is the cooling device shown in Figure 2. This rather simple device consists of a 1/4-inch copper tubing cooling water loop to which a loop of braided copper strap is hard-soldered. The capsule cap seats into the strap loop and the copper provides a good heat conduction path to the cooling water line. A typical cooling curve of a capsule cap is shown in Figure 3. With this device the entire capsule can be cooled from 1200°C to below the melting point of potassium (62°C) in less than 20 minutes. With the chill block assembly, the capsule required an over night cooling period to reach this temperature.

During the early part of the quarter, the transfer of potassium from the space inside the crucible-collector sub-assembly to the outside was a serious problem. Because of the uncertainties associated with the interpretation of the solute analysis and the evaluation of the solubilities when the potassium transfers, a number of techniques for effecting a mechanical seal were tried. However, the desire to maintain and preserve the integrity of the single crystal crucibles restricted the choices of

possible techniques to those which would not damage the crucible material. The techniques used in our attempts to control the transfer during this period have been: 1) the use of a solid spacer inside the capsule such that the top of the collector was supported at a level slightly above the lip of the crucible at the time the welding cap was attached, 2) the use of a matching low-angle bevel on the collector and on the crucible to form a tapered joint, and 3) sealing the capsule with a compressed coil spring beneath the crucible-collector sub-assembly so that the sealing force would continue to be applied to the tapered joint during the test period. In addition to these attempts to develop a tight joint, an adjustment of the temperature gradient along the capsule was made to minimize the tendency for the potassium to transfer during the test.

None of these techniques has been uniformly successful in preventing the transfer of potassium. The reduction of the temperature gradient is thought to help, and we are now routinely operating with a maximum axial ΔT of 3-6°C, depending upon the temperature level of the test. The bottom of the capsule, and, presumably, the single crystal crucible also, are characteristically the coldest. This is believed to favor the retention of the potassium in the crucible during the test period, because with the potassium vapor pressure lowest at the bottom, the tendency to condense elsewhere is minimized.

The tapered joint between the collector and the crucible was expected to help in retaining the potassium by forming a mechanical seal. However, the potassium does transfer unless the joint becomes a metallurgical bond. Thus far, the only good sintered joints have been made when solid spacers were used. In these cases, nearly all of the potassium loaded into the crucible was found in the collector, and the joint had to be forcibly separated. However, the number of sintered joints that have formed is small. One reason for this may be that the test temperatures may be too low to encourage sintering. Another reason may be that the spacer does not maintain a steady force on the collector-crucible sub-assembly during the entire run. At the beginning, all of the internal parts expand during heating. Since the usual collector is tantalum, and because tantalum has a greater expansion coefficient than molybdenum, an expansion-induced axial force develops during

the initial approach to the test temperature. During the higher temperature runs in particular, the axial stress in the tantalum may exceed its short time compressive yield strength and it may plastically deform. Then, as the test proceeds at constant temperature (whether there has been previous yielding or not), the tantalum collector will tend to undergo plastic deformation as controlled by its creep properties, and, as a result, the stress level in the collector will decrease with time. Then, as the test is ended and the capsule cools, there is at first a compression action on the tapered joint, followed by a relaxation of stress to zero, as the contraction of the now-deformed tantalum exceeds that of the molybdenum capsule.

The result of this sequence is that the sealing force on the crucible-collector joint could vary by a large factor during the test period, and it seems inevitable that the force must drop to zero during the quench period. Thus, unless sintering occurs near the start of the test, the loss of potassium during the quench operation seems quite likely.

The use of a compressed spring was initiated in an attempt to avoid the problem described above. It was intended that the spring would be compressed to, say, 2 to 3 lbs during welding, and would continue to apply that force during the heating period until its modulus began to decrease. The spring is the most heavily stressed element in the capsule and it is expected to be subject to creep. Accordingly, the applied force will decrease during the test and, if the creep is excessive, the spring action may fail. In this case, the spring is no more effective than the solid spacer. On the other hand, if a creep-resistant spring metal can be used, it will maintain a force on the crucible-collector joint through the entire test period, and, even if sintering of the joint does not occur, the spring may hold the tapered joint together so the potassium transfer is minimized.

Refractory alloy springs have been used in this application. The springs were made of nine turns of 25-30 mil wire, and were 7/8 inch long and 3/8 inch in diameter. The springs were placed beneath the crucibles and collectors in the assembly of the capsules, as shown in the exploded view of a capsule and contents in Figure 4. Before the capsule cap was put in place, the top of the collector extended about 3/8 inch above the top of the capsule. Thus far, three spring materials have been used and all have been found to be

unsatisfactory. These are: tungsten, the niobium-base alloy C-129Y, (Nb-10W-10Hf-0.2Y) and the tantalum base alloy T-111 (Ta-8W-2Hf). The tungsten springs were used at 600°, 800°, 1000°, and 1100°C for test periods up to eight hours. In all cases, the springs were found to be collapsed when the capsules were opened. The C-129Y springs were used at 800°, 1000°, and 1200°C for periods up to eight hours. In all cases the C-129Y springs had relaxed so that they just filled the space, but they did not appear to be applying any force. The C-129Y springs were brittle after use, and one of them fractured into several parts when it was subsequently compressed. The T-111 springs were also used at 800°, 1000°, and 1200°C for 8 hours. In all cases the T-111 springs had relaxed so that they filled the available space inside the capsules, but little or no force was being applied. These T-111 springs, though shortened, did continue to possess spring-like qualities and could be flexed without damage.

Although all of the various springs relaxed during the tests, the amount of potassium transferred varied. In some cases, a large fraction of the potassium was retained in the crucible-collector assembly, but in other cases most of the potassium escaped to the exterior of the crucible. Tables 1, 2, and 3 summarize the results of the tests performed during the quarter. In addition, pertinent data from the previous quarterly report is included in the tables for convenience. An examination of the amounts of potassium found in the crucibles shows that the greatest percentage retained in these attempts to form a mechanical seal was 74%. The least amount found in the collector was 5% of the amount loaded. These observations clearly demonstrate the inability of the mechanical joint to retain the potassium within the crucible-collector sub-assembly.

From the results of the various tests carried out, it became obvious that some means other than spacers and/or springs must be used to form a seal. The only method which now seems feasible is the use of a braze or a weld to effect the seal. The choice between these two sealing techniques was made on the basis that the braze joint requires the use of a lower temperature, which minimizes the heating of the potassium in the crucible. It is feared that the use of welding temperatures for molybdenum and niobium (which temperatures are above 2500°C) would be quite likely to cause the volatilization and loss of the potassium in the crucible. An additional

consideration was the fact that a welding operation would almost certainly destroy the single crystallinity of the crucible in the region of the weld, and would thereby severely limit the number of times a given crucible could be re-used. The braze seal, however, allows the use of a much lower seal temperature (about 1600°C for a nickel braze, and 1900°C for a zirconium braze) and lowers the probability of the loss of potassium by volatilization. For this reason, the lower sealing temperatures are strongly preferred. Further, the use of a braze is less damaging to the crucible and would allow its re-use for a greater number of tests than would be possible with a welded joint. We have deliberately avoided this sort of closure in the past because of the concern about contaminating the single crystal crucibles with the braze metal, but it now appears to be the only way of effecting the required seal. The braze metal chosen for the first tests was nickel. The procedure involves electroplating nickel on the upper portion of the 5° taper which is machined on the sample collector. The last 1/16" of the taper is masked to prevent deposition there and thereby to reduce the chance that nickel would be dissolved in the potassium. A typical plated collector is shown in Figure 5. The amount of nickel used is 25 to 30 mg, giving a plate about 0.001" thick on the tantalum. The plated collector is mated to the taper on the sample crucible, and the braze is effected by heating the joint area above the melting point of nickel, while a weight on the collector maintains a tight joint as the nickel softens.

The concern that the nickel braze would interact with the potassium and complicate the interpretation of the experimental results was allayed by the finding that no nickel was detected in any of the solvents tested.

Identical brazed joints have been made to join tantalum crucibles to molybdenum sample collectors, with the nickel plate being applied to the molybdenum. An alternate braze metal which may be considered, if necessary, is zirconium. A nickel braze was attempted to join iron crucibles to tantalum collectors, but the melting points of iron and nickel were found to be too close together to permit the use of nickel as the braze metal for these crucibles. The use of copper, applied as a loop of wire which is melted to form a fillet at the outer interface of the tapered joint, appears satisfactory. The melting point of copper limits the operating temperature of experiments in which this braze is used to about 1000°C.

Table 1. Summary of Experimental Data for Iron

#	T °C	Time, hr	Results	Comments
(Repeated from Sixth Quarterly)				
314	800	2.6	11 ppm Fe	40 ppm O in K; Zr getter in crucible; 76% of K in collector; analysis based on total K.
317	800	8.0	17 ppm Fe	16 ppm O in K; Zr getter in collector; 65% of K in collector; analysis based on total K.
318	800	8.0	15 ppm Fe	16 ppm O in K; 45% of K in collector; analysis based on total K.
320	800	4.0	21 ppm Fe	16 ppm O in K; 55% of K in collector; analysis based on estimated total K.
327	1000	2.0	51 ppm Fe	16 ppm O in K; 63% of K in collector; analysis based on total K.
332	1000	4.0	43 ppm Fe	16 ppm O in K; 20% of K in collector; knife-edge; analysis based on total K.
333	1000	4.0	70 ppm Fe	16 ppm O in K; 98% of K in collector; knife-edge; formed diffusion bond seal; analysis based on total K.
336	1200	2.0	500 ppm Fe	16 ppm O in K; knife-edge, analysis based on total K.
(Data Obtained in Current Quarter)				
343	1200	4.0	325 ppm Fe	14 ppm O in K; 27% of K in collector, 10° taper; analysis based on measured K loaded into crucible.
344	1000	8.0	9 ppm Fe	14 ppm O in K; 60% of K in collector, 10° taper, some bonding occurred; analysis based on measured K loaded into crucible.
349	1000	8.0	13 ppm Fe	14 ppm O in K; 32% of K in collector, W spring, 7° taper, some bonding in joint; analysis based on measured K loaded into crucible.

Table 1 (Continued)

#	T °C	Time, hr	Results (Data Obtained in Current Quarter)	Comments
350	1000	8.0	12 ppm Fe	14 ppm O in K; only 3% of K in collector; W spring, 7° taper; analysis based on measured K loaded into crucible.
154	600	7.3	6 ppm Fe	Power failure during run; 14 ppm O in K; 48% of K in collector; W spring; 5° taper.
155	800	8.0	5 ppm Fe	14 ppm O in K; 3% of K in collector; W spring; 5° taper.
159	1000	8.0	9 ppm Fe	14 ppm O in K; 10% of K in collector; C-129 alloy spring; 5° taper.
160	800	8.0	9 ppm Fe	14 ppm O in K; 23% of K in collector; C-129 alloy spring; 5° taper; analysis based on measured K loaded into crucible.
165	800	8.0	Fe*	14 ppm O in K, T-111 alloy spring, 5° taper.
172	800	4.0	Fe*	14 ppm O in K; Ni braze; 5° taper; braze joint was not tight, but most of K remained in collector.
182	800	8.0	Fe*	14 ppm O in K, Cu braze, 5° taper.

*Analysis not yet complete.

The results obtained for the iron solubility tests performed during the quarter are summarized in Table 1, and are plotted in Figure 6. All of the data obtained in tests in which about 50% of the potassium was retained in the collector as shown on the Figure. The reason for the apparent low value obtained for run 344 is not understood. There was no reason to doubt the integrity of the test procedure in this test, and the chemical analysis was performed in a group of three which also included runs 349 and 350. The results for these runs are not shown because less than 50% of the potassium was found in the collectors. Although there is no other reason to suspect the analytical procedure, it has been established that in these three analyses an HCl wash was used instead of the usual HNO_3-HF wash used in the other analyses.

The result found in run 154 appears to be high, with respect to the extrapolation of the dashed line shown on Figure 6. The test was prematurely terminated because of power source difficulties but there was some advance warning, and the test was terminated normally.

The dashed line which represents the remainder of the data in Figure 6 is substantially the same line as that shown in the previous Quarterly Report[1]. From the present data, one must conclude that there is little, if any, indication that equilibrium solution values are not attained in two hours' exposure. The dashed line which represents the bulk of the data shown on Figure 6 has a slope which corresponds to a ΔH(solution) of 25,000 cal/mol. This compares with the value of 28,200 cal/mol reported by Swisher[2] for the solution of commercially pure iron in potassium containing about 20 ppm oxygen.

The results obtained for the niobium solubility tests performed during the quarter are summarized in Table 2 and are plotted in Figure 7. The data indicate the usually expected trend of solution data with temperature, although there are at present too few data points to warrant drawing a "best-fit" curve.

The results obtained for the molybdenum solubility tests performed during the qarter are summarized in Table 3, and are plotted in Figure 8. The data show the expected trend with temperature, but the scatter is large.

Table 2. Summary of Experimental Data for Niobium

#	T °C	Time, hr	Results	Comments
346	1200	4.0	-	Thermocouples sintered to capsule. TZM shaft was broken during inversion. No analysis made.
156	1100	8.0	17 ppm Nb	14 ppm O in K; 20% of K in collector; W spring; 5° taper; slight bonding in joint; analysis based on measured K loaded into crucible.
161	1200	4.0	-	14 ppm O in K, C-129 alloy spring, 5° taper, noticeable bonding in joint, no K in collector, no analysis made.
169	1200	8.0	34 ppm Nb	14 ppm O in K; Ni braze; 5° taper; analysis based on K in collector.
171	1000	8.0	15 ppm Nb	14 ppm O in K; Ni braze; 5° taper; analysis based on K in collector.
174	1000	4.0	66 ppm Nb	14 ppm O in K; Ni braze; 5° taper; imperfect braze joint; analysis based on estimated K loaded into crucible.
175	1100	8.0	12 ppm Nb	14 ppm O in K; Ni braze; 5° taper; some evaporation of K during brazing operation, estimate about half was lost, but joint was tight; analysis based on K in collector.
179	1000	2.0	Nb*	14 ppm O in K; Ni braze; 5° taper; imperfect braze.

*Analysis not yet complete.

Table 3. Summary of Experimental Data for Molybdenum

#	T °C	Time, hr	Results	Comments
345	1200	4.0	207 ppm Mo	14 ppm O in K; 22% of K in collector, 10° taper; analysis based on measured K loaded into crucible.
152	1000	8.0	19 ppm Mo	14 ppm O in K; 17% of K in collector; W spring, 5° taper, single crystal Mo crucible; analysis based on measured K loaded into crucible.
153	1100	8.0	17 ppm Mo	14 ppm O in K, 48% of K in collector; double W spring, 5° taper, some bonding in joint; analysis based on measured K loaded into crucible.
158	1200	4.0	35 ppm Mo	14 ppm O in K; 43% of K in collector; Mo spacer; 5° taper; analysis based on measured K loaded into crucible.
163	1000	8.0	1.6 ppm Mo	14 ppm O in K; 74% of K in collector; T-111 alloy spring; 5° taper; analysis based on measured K loaded into crucible.
164	1200	8.0	121 ppm Mo	14 ppm O in K; 31% of K in collector; T-111 alloy spring; 5° taper; analysis based on measured K loaded into crucible.
166	1200	4.0	14 ppm Mo	14 ppm O in K; Ni braze; 5° taper; analysis based on K in collector.
167	1200	8.0	13 ppm Mo	14 ppm O in K; Ni braze; 5° taper; analysis based on K in collector.
168	1200	2.0	8.2 ppm Mo	14 ppm O in K; Ni braze; 5° taper; imperfect braze joint; analysis based on measured K loaded into crucible.
173	1000	8.0	4.3 ppm Mo	14 ppm O in K; Ni braze; 5° taper.
176	1000	4.0	2.6 ppm Mo	14 ppm O in K; Ni braze; 5° taper.
177	1100	8.0	1.4 ppm Mo	14 ppm O in K; Ni braze; 5° taper.
178	1000	2.0	Mo*	14 ppm O in K; Ni braze; 5° taper.

*Analysis not yet complete.

This may be due, in part, to the variable blank corrections which are observed from one collector to the next; and in part to a possible interference in the analysis between the tantalum from the collector and the rather small amounts of molybdenum present in the potassium. Because of these uncertainties, the data must be considered tentative, until a resolution can be made.

In addition to the tests made on iron, niobium, and molybdenum, there were two tests performed on the recently-received tantalum crucible, using the nickel braze technique. These were done at 1000°C for 8 hours and for 4 hours, respectively. The analyses are not yet complete because an interference in the colorimetric analysis for tantalum was found in the presence of the relatively large amounts molybdenum (0.1-0.2 grams) which are removed from the collector to ensure recovery of all of the dissolved tantalum. In these analyses, therefore, there may be 10,000 times as much molybdenum as tantalum, and a very selective and effective separation of the two elements must be effected before the tantalum analysis can be a meaningful one.

An examination of Tables 1, 2, and 3 indicates that the nickel braze techniques has not always produced a tight joint. It is believed that, in the cases in which the joint leaked, the temperature of the joint during the sealing operation was too low, or the time was too short, to allow the nickel to wet the adjacent metals. The frequency of the formation of poor joints has markedly decreased as more experience in making them is gained.

A second aspect of the nickel braze joint is the question of the exposure and possible solution of nickel in the solvent potassium. In order to test for the solution of nickel in the potassium, analyses were made in tests 173, 176, and 177 and no nickel (<1 ppm) was detected in any of them. This, plus the fact that the nickel plating is very thin and is not carried to the tip of the collector, suggests that no contamination of the test systems by nickel should be caused by a properly brazed joint.

Material Procurement, Preparation, and Characterization

Six single crystals were submitted to Sifco for electrochemical machining to form crucibles. These have all been returned and are in use

in the testing program. One of the two niobium single crystal crucibles was prepared entirely by Sifco's electrochemical machining (ECM) technique. The second niobium crucible was prepared by forming an undersized hole using the Elox technique. Then the hole was electrochemically machined to the design diameter and depth. The first molybdenum crucible was prepared by the ECM process, but the second one was prepared by the Elox followed by the ECM techniques. Because of the delay in obtaining the second molybdenum crucible, a third crucible was prepared from a single crystal molybdenum by mechanically drilling an undersized hole in it, and by using a heavy electropolishing treatment to finish the cavity. Both of the niobium crucibles and all three of the molybdenum crucibles are currently in use in the experimental program.

Neither of the two tantalum single crystals was machined by Sifco. They had intended to use the Elox plus the finishing ECM technique but were unable to meet the delivery schedule and returned the crystals without treatment. These crystals were made into crucibles by the combination of mechanical machining and electropolishing.

Table 4 lists the double layer capacitance (DLC) values measured for all of our crucibles. An examination of the ratio of the DLC area and the geometric area indicates that the electropolishing treatment given the crucibles produces a very smooth surface which is nominally equal to the geometric area, within the uncertainty of the DLC measurement itself ($\pm$ 10%).

Table 4. Double Layer Capacitance Values for Solute Samples

Material	Geometric Area, A_G cm^2	DLC Area, A_D cm^2	Ratio A_D/A_G
Fe-1	20.6	19.6	0.952
Fe-2	19.2	20.8	1.082
Mo-1	18.82	20.4	1.082
Mo-2	18.38	19.8	1.078
Nb-1	16.46	15.45	0.938
Ta-1	16.56	15.24	0.921
Ta-2	17.47	18.22	1.044

The third batch of purified potassium was prepared. The process involved the draining of the remainder of the second batch of potassium from the extruder, and the normal sequence of filtering, hot gettering, and distillation of the new batch. Table 5 shows its analysis. It is of interest to note that the oxygen level is decreasing from batch to batch, i.e., successive levels have been 40-70, 16, and 14 ppm O.

Table 5. Analysis of Third Batch of Potassium*

Element	Analysis, ppm	Element	Analysis, ppm	Element	Analysis, ppm
Ag	<1 ND	Co	<10 ND	Na	5 D
Al	1 D	Cr	<1 ND	Ni	<2 ND
B	<10 ND	Cu	<2 ND	Pb	<1 ND
Ba	<10 ND	Fe	<2 ND	Sn	<5 ND
Be	<1 ND	Li	<1 ND	Ta	<2 ND
Bi	<1 ND	Mg	3 D	Ti	<20 ND
Ca	<5 D	Mn	<2 ND	V	<1 ND
Cd	<1 ND	Mo	<2 ND		
O	13, 13, 16 Avg = 14				

*Spectroscopic values except for O (mercury amalgamation) and Ta (colorimetric).

An experiment designed to evaluate the rate of contamination of an exposed surface of potassium by open exposure to the nominal $(1\text{-}3)\times10^{-7}$ Torr atmosphere in the vacuum system has been carried out. Four weighing bottles were loaded with solid potassium and exposed to the vacuum atmosphere for two days. The potassium was then analyzed for the oxygen absorbed. The results of this study are summarized in Table 6, which indicates the average oxygen contamination rate to be 0.1135 $\mu gm/cm^2/hr$.

Table 6. Summary of Oxygen Contamination Rate Experiments*

Effective Area cm^2	Net Oxygen Absorbed μgm		Absorption Rate $\mu gm/cm^2/hr$ (48 hr test)
3.47	27.9		0.168
4.92	32.1		0.132
4.92	25.8		0.109
5.66	12.3		0.045
		Avg	0.1135
		Avg Dev	0.0365

* P = 3×10^{-7} Torr - without liquid nitrogen trapping.

Thus the estimated amount of oxygen contamination of a standard 1.5-2.0 gm sample having about eight cm^2 of exposed area is less than 0.5 μgm during normal crucible loading. Normally, the time of exposure to the liquid nitrogen trapped atmosphere at $(1-3) \times 10^{-7}$ Torr is less than 30 minutes.

IV. NEXT REPORT PERIOD ACTIVIES

During the next quarter, the major efforts will be directed toward continuing experimental measurements on the tantalum, niobium, molybdenum and iron samples, with emphasis on establishing the solubility values, and on the determination of the solution kinetics of niobium and tantalum.

V. PROJECT REPORTS ISSUED ON THIS CONTRACT

R. L. McKisson, R. L. Eichelberger, and J. M. Scarborough, "Solubility and Diffusion Studies of Ultra Pure Transition Elements in Ultra Pure Alkali Metals," First Quarterly Report, AI-9151, November 6, 1963.

R. L. McKisson, R. L. Eichelberger, and G. R. Argue, "Solubility and Diffusion Studies in Alkali Metals," Second Quarterly Report, AI-64-5, February 7, 1964.

R. L. McKisson, R. L. Eichelberger, G. R. Argue, and J. M. Scarborough, "Solubility and Diffusion Studies in Alkali Metals," Third Quarterly Report, NASA-CR-54043 (AI-64-75), May 11, 1964.

R. L. McKisson, R. L. Eichelberger, G. R. Argue, and J. M. Scarborough, "Solubility and Diffusion Studies in Alkali Metals," Fourth Quarterly Report, NASA-CR-54094 (AI-65-156), August 10, 1964.

R. L. McKisson and R. L. Eichelberger, "Solubility and Diffusion Studies in Alkali Metals," Fifth Quarterly Report, NASA-CR-54095 (AI-64-235), November 16, 1964.

R. L. McKisson and R. L. Eichelberger, "Solubility and Diffusion Studies in Alkali Metals," Sixth Quarterly Report, NASA-CR-54096 (AI-65-15), March 5, 1965.

VI. AI INTERNAL REPORTS ISSUED ON THIS CONTRACT

G. R. Argue, W. A. McCollum, and H. L. Recht, "Double Layer Capacitance Measurements on Ta, Mo, and Nb," AI-TDR-9773, March (1964).

R. L. McKisson, "Analysis of the Freezing Point Depression Technique of Determining Impurity Content of Alkali Metal," AI-TDR-9404 (March, 1964).

G. R. Argue, H. L. Recht, and W. A. McCollum, "Double Layer Capacitance Measurements on Iron Crucibles to Determine Surface Area," AI-TDR-64-229.

VII. REFERENCES

1. R. L. McKisson and R. L. Eichelberger, "Solubility and Diffusion Studies of Ultra Pure Transition Elements in Ultra Pure Alkali Metals," Sixth Quarterly Report, NASA-CR-54096, AI-65-15, March 5, 1965.

2. J. H. Swisher, "Solubility of Iron, Nickel, and Cobalt in Liquid Potassium and Effect of Oxygen Gettering Agents on Iron Solubility," NASA-TN-2734, March, 1965.

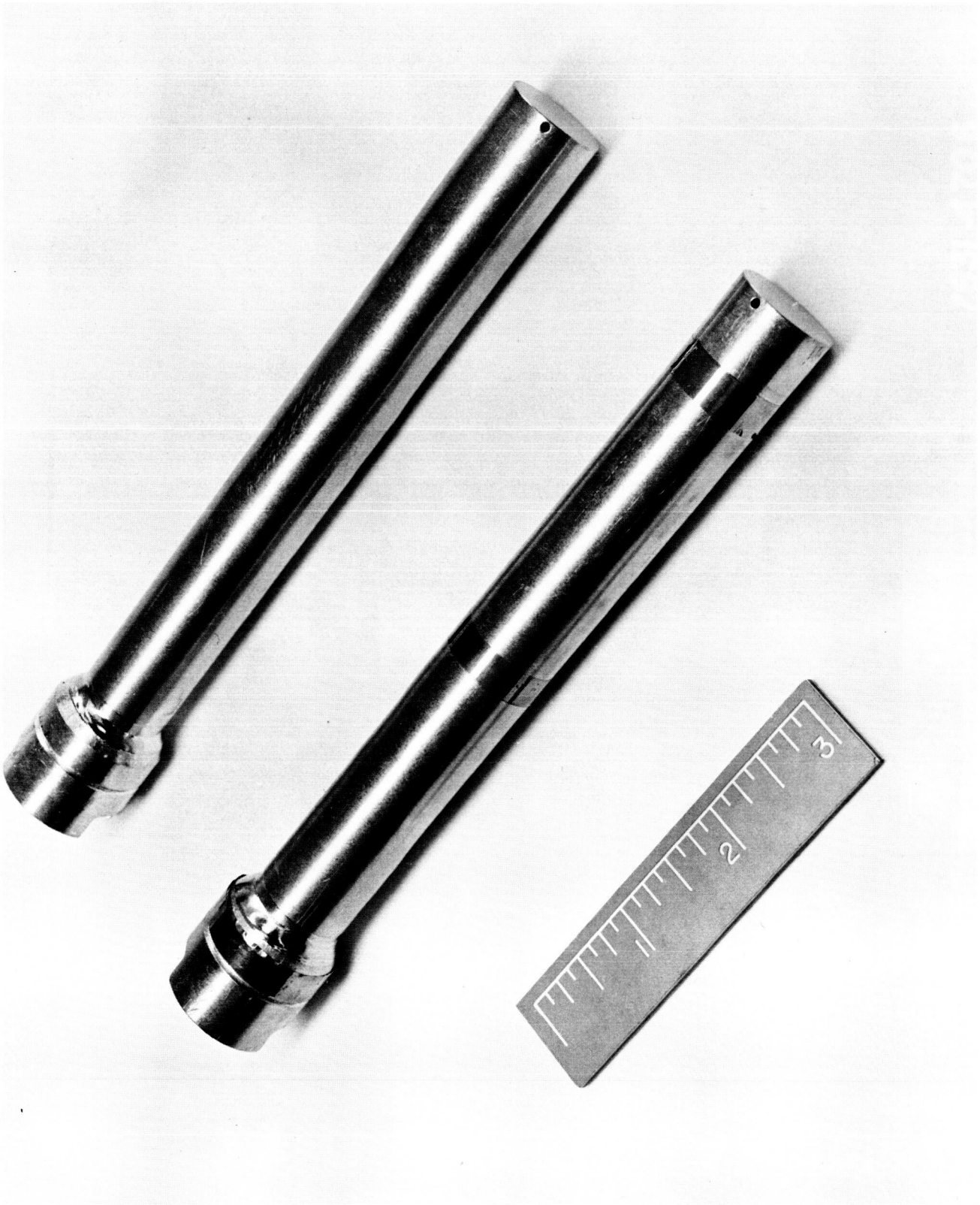

FIGURE 1. WELDED CAPSULE

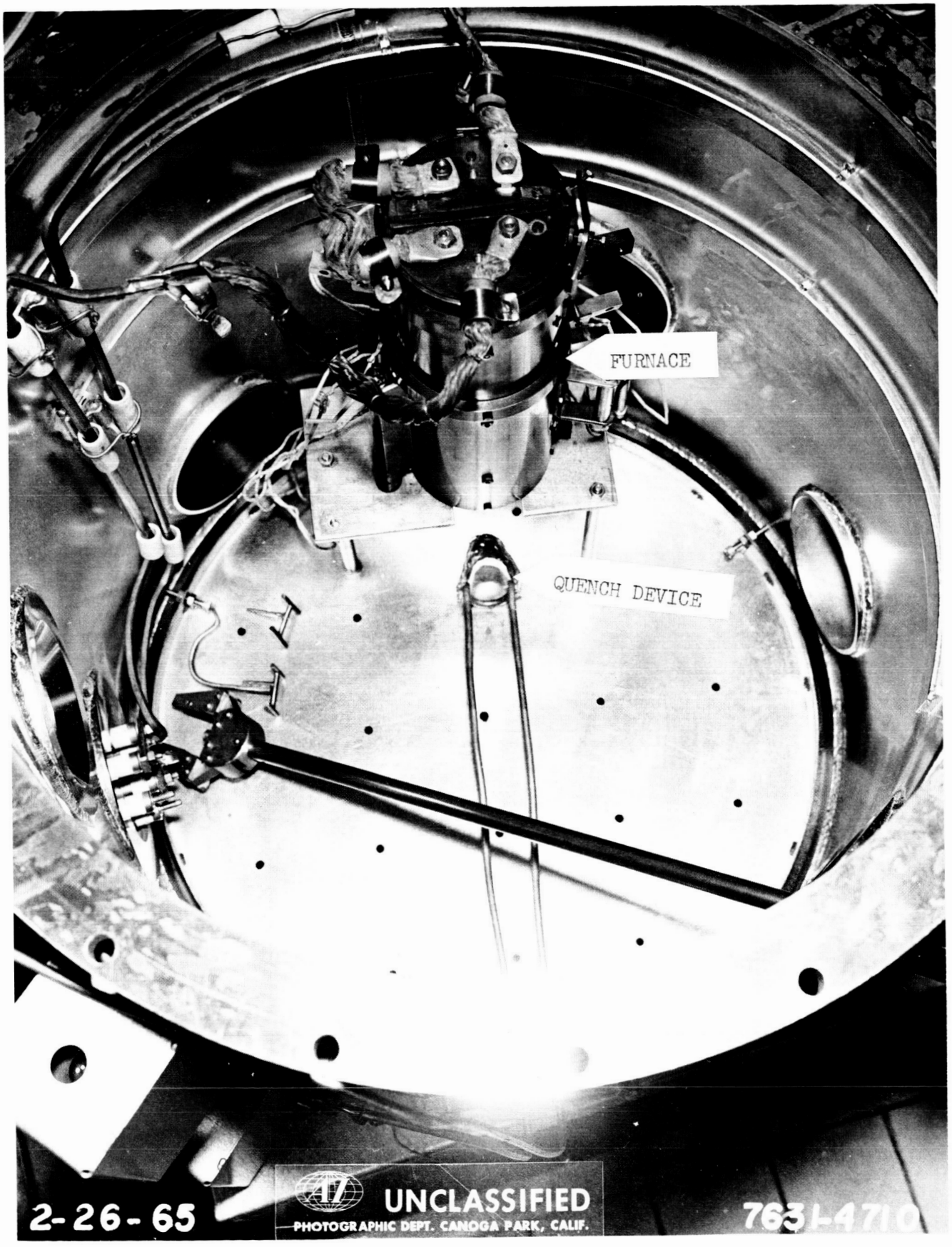

FIGURE 2. FURNACE, SHOWING WATER COOLED QUENCH DEVICE

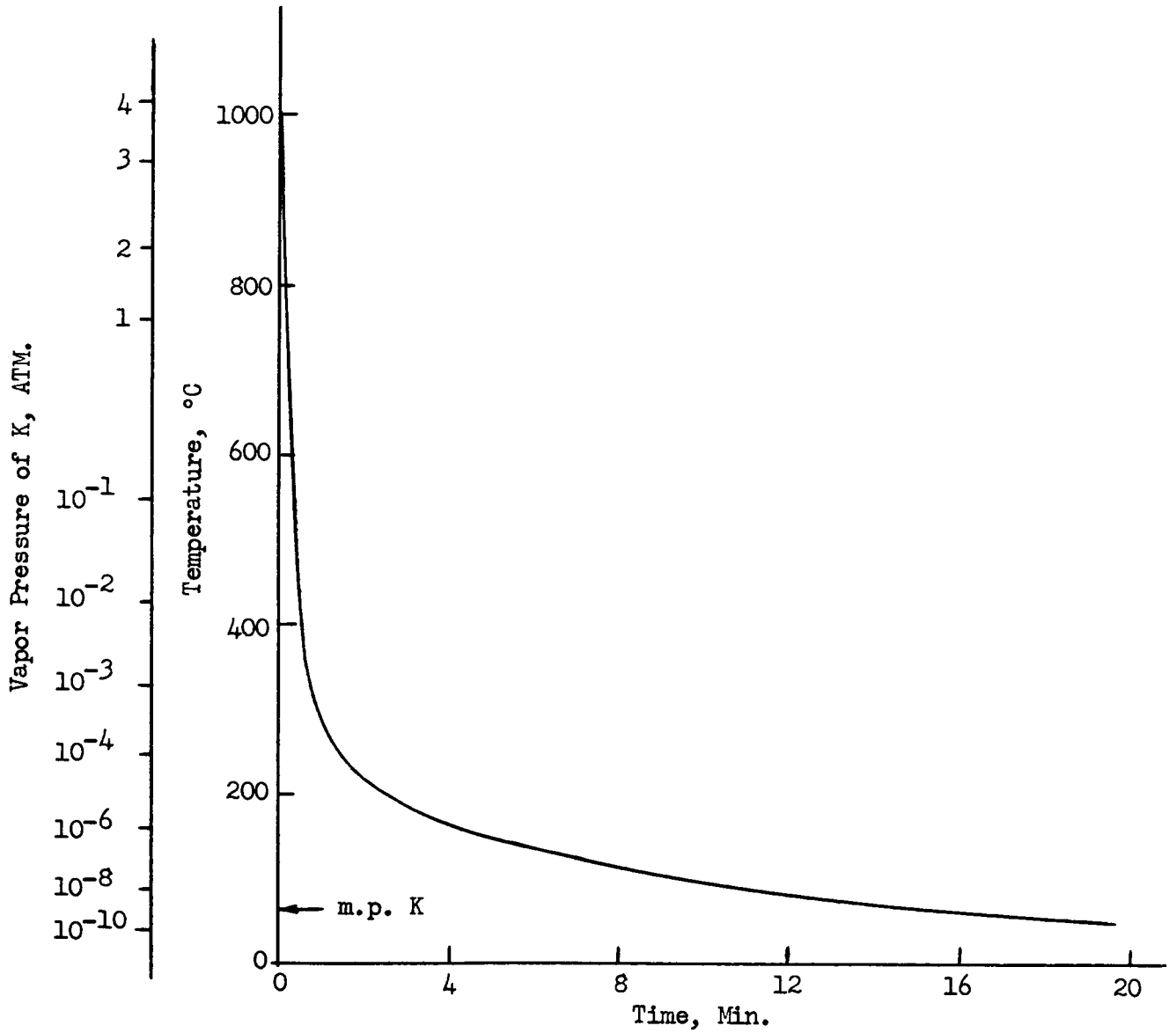

Figure 3

Quenching Curve Using Water Cooled Quench Device

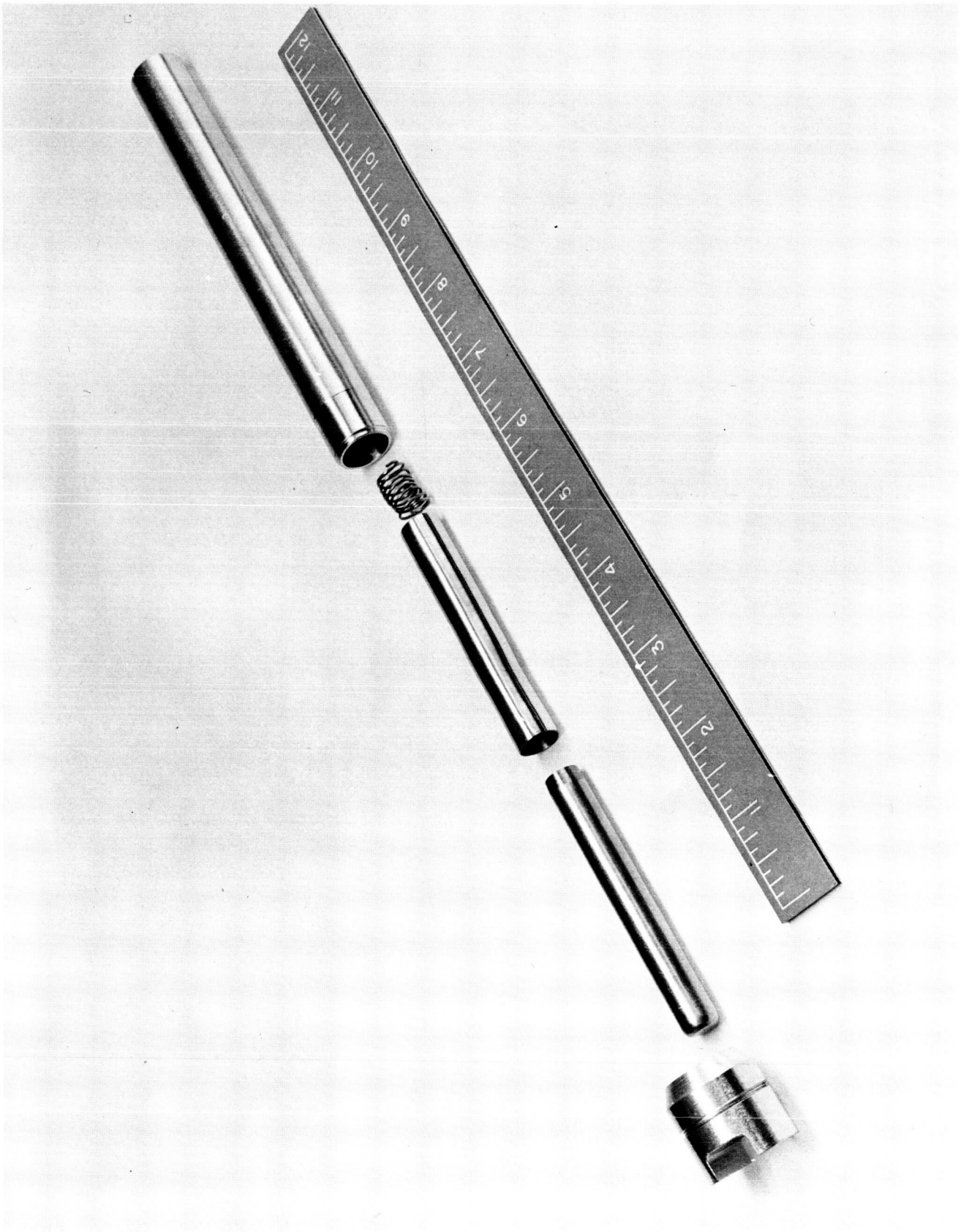

FIGURE 4. EXPLODED VIEW OF THE CAPSULE ASSEMBLY

FIGURE 5. COLLECTOR, SHOWING ELECTROPLATED NICKEL BRAZE METAL

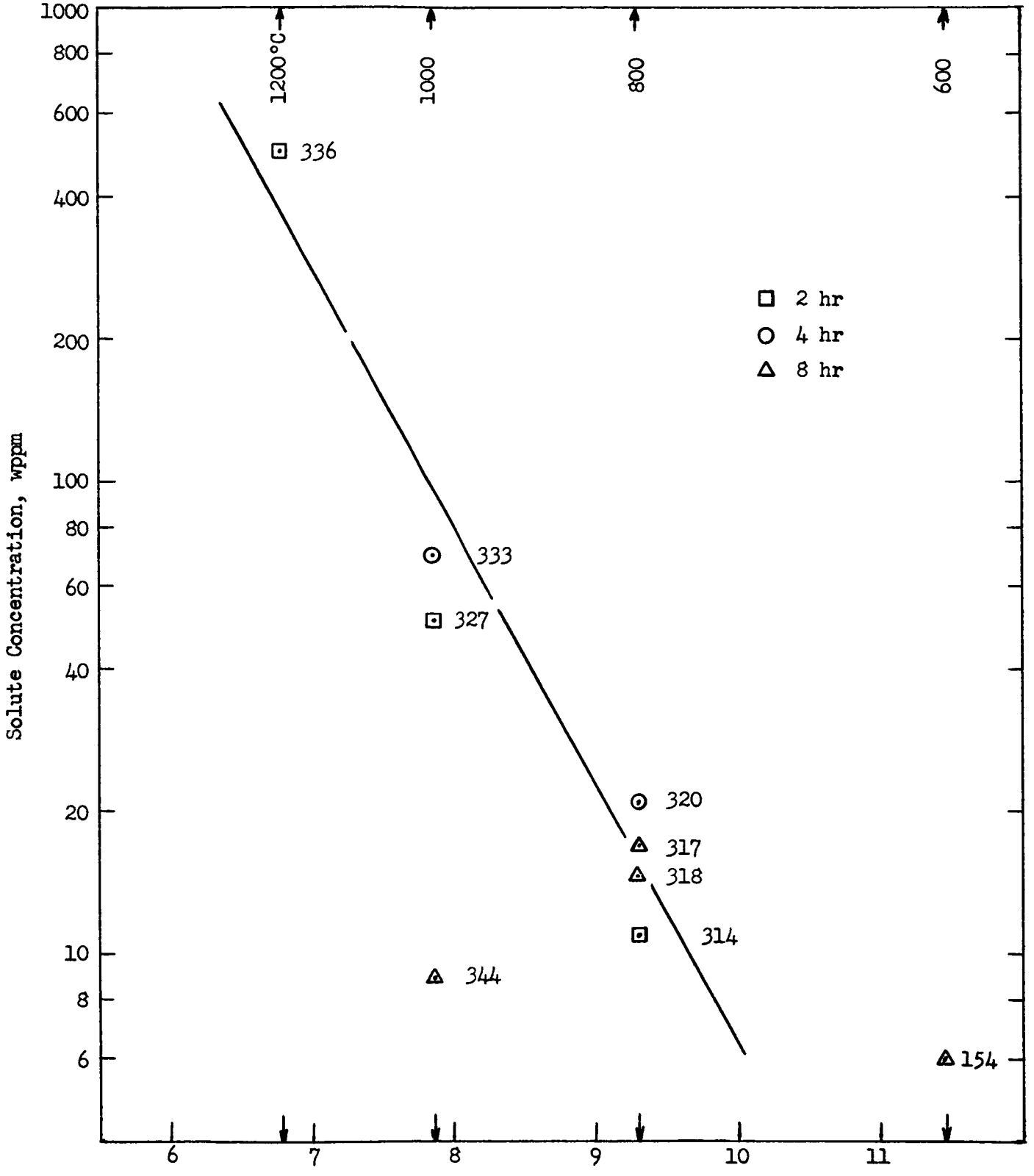

Figure 6

Concentration of Iron Solue Dissolved in Potassium
Containing 14-16 wppm Oxygen

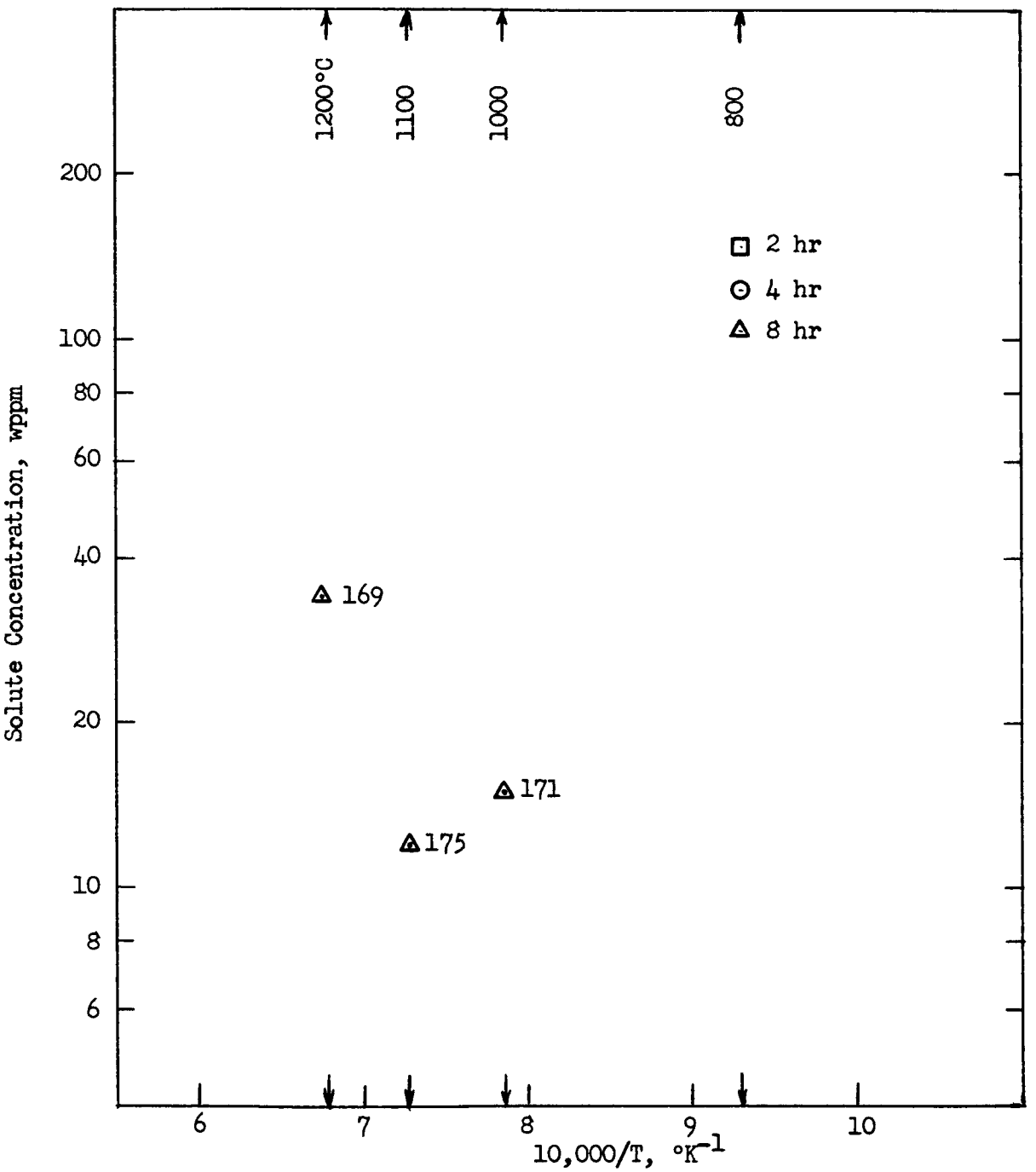

Figure 7

Concentration of Niobium Solute Dissolved
in Potassium Containing 14 wppm Oxygen

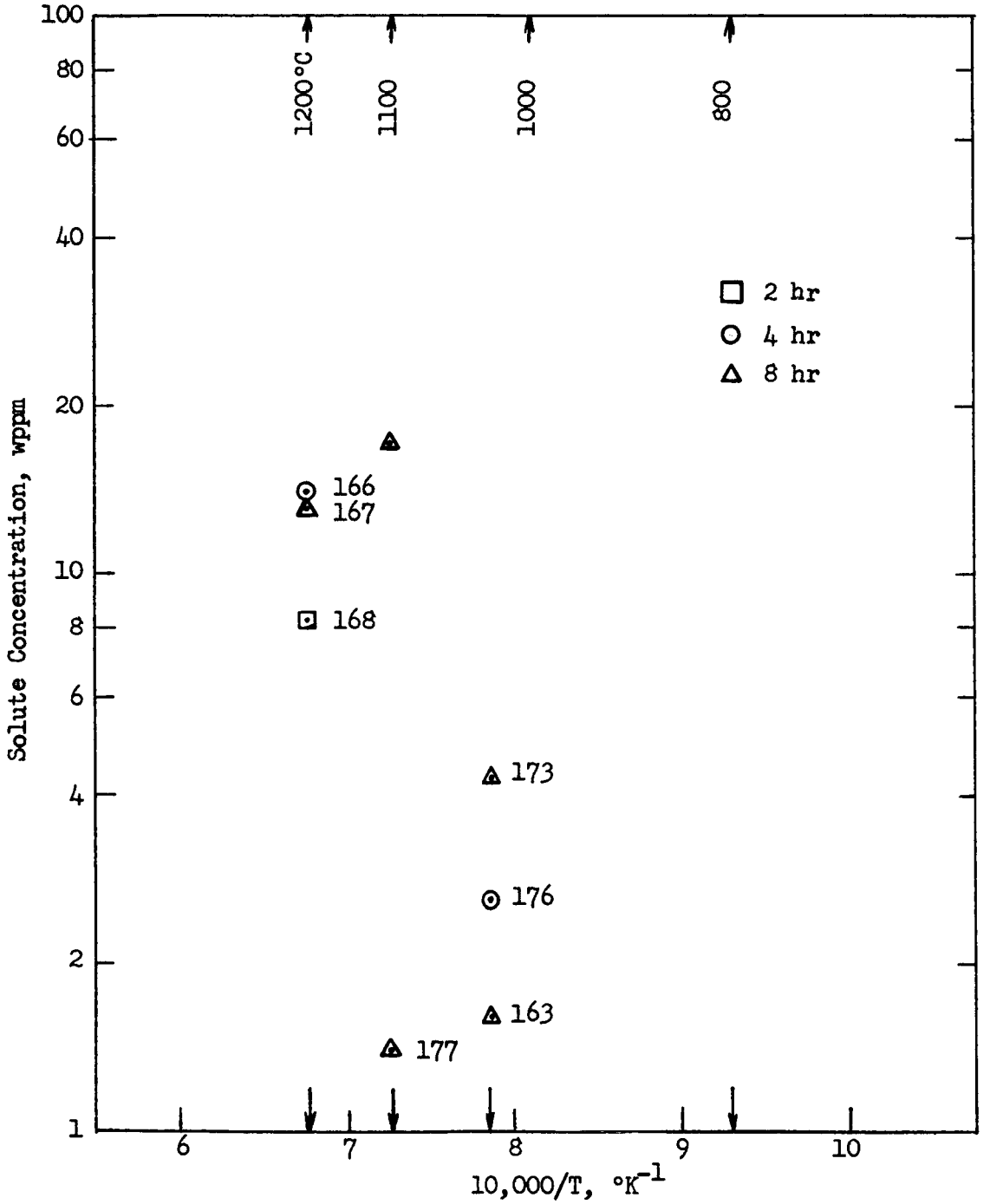

Figure 8

Concentration of Molybdenum Solute Dissolved in Potassium Containing 14 wppm Oxygen